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Indoor surface chemistry: ozone reaction with nicotine sorbed to model materials.

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Abstract

The interaction of ozone with nicotine sorbed to Teflon or cotton surfaces was investigated in an environmental chamber by monitoring nicotine desorption over a week following equilibration in dry or humid air (65-70 % RH). The Teflon and cotton surfaces had N₂-BET surface areas of 0.19 and 1.17 m² g⁻¹, and water mass uptakes (at 70 % RH) of 0 and 7.1 % respectively. In dry air, gas phase nicotine concentrations decreased with respect to baseline (no O₃) levels by 2 orders of magnitude for Teflon after 50 h at 20–45 ppb O₃, and by a factor of 10 for cotton after 100 h with 13–15 ppb O₃. The ratios of pseudo first-order rate constants for surface reaction (r) to long-term desorption (k) were $r/k = 3.5$ and 2.0 for Teflon and cotton surfaces, respectively. Formaldehyde, N-methylformamide, nicotinaldehyde and cotinine were identified as oxidation products, indicating that the pyrrolidinic N was the site of electrophilic attack by O₃. The presence of water vapor had no effect on the nicotine-O₃ reaction on Teflon surfaces. By contrast, nicotine desorption profiles from cotton in humid air were identical in the presence or absence of ozone. The latter phenomenon is ascribed to complete inhibition of ozone-nicotine surface reactions by co-sorbed water through decomposition of ozone in the aqueous surface film and/or interactions of nicotine with water that reduced its reactivity towards ozone. Oxidative losses of sorbed nicotine and reduction in its re-emission could attenuate possible biases in use of nicotine as a tracer for environmental tobacco smoke.

Introduction

(S)-(-)-Nicotine, the principal alkaloid in tobacco, is emitted in the sidestream and exhaled mainstream smoke of cigarettes¹⁻³. It is commonly used as a tracer for environmental tobacco smoke (ETS, also known as secondhand smoke) in indoor environments⁴⁻⁷, and its metabolite cotinine is widely utilized as a biomarker in epidemiological and intervention studies. Cotinine is considered a very sensitive and specific ETS biomarker, due to its high concentrations in urine (up to 50 ng mL⁻¹) and to the fact that nicotine, its precursor, is essentially exclusive to tobacco, thus avoiding potential confusions with other coexisting pollutant sources^{2, 8, 9}. However, the assessment of secondhand smoke exposure using nicotine and nicotine-related tracers is complicated by the fact that non-smokers' exposure to nicotine and other nonsorbing toxic gases and aerosol particles present in ETS are often partially uncorrelated as a consequence of their very different indoor dynamics¹⁰⁻¹². Nicotine has been observed to bind to surfaces, and then re-emit to indoor air over periods that can extend from days to weeks following the smoking event. Significant experimental and modeling efforts¹³⁻¹⁶, together with field studies¹⁶, have aimed at better understanding and characterizing how sorption and desorption from indoor materials affect the composition of ETS and the suitability of nicotine as a tracer. Here, the term *sorption*¹⁷ describes the binding of a sorbate to material surfaces through physisorption, chemisorption, dissolution into liquid coating films and/or diffusion into porous matrices. Nicotine and its metabolites have been found to be good ETS markers in environments where smoking occurred regularly and the data were averaged over long periods, but they did not predict exposures on short time scales or when smoking was infrequent and irregular^{10, 14, 16}.

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More recently, studies performed in a furnished model room incorporated sorption effects into the calculation of exposure-relevant emission factors^{18, 19}.

Despite experimental evidence of its strong sorption to indoor surfaces, very little is known about the reactivity of sorbed nicotine. Most scenarios for long-term desorption from indoor surfaces assume that sorbed nicotine is chemically inert over residence times of several days to weeks. If nicotine reacts with indoor species this assumption could lead to overestimation of re-emission rates.

Oxidation by atmospheric species is the most likely chemical process involving sorbed nicotine. The oxidation of nicotine has been studied under a variety of conditions for the past 90 years, following the seminal 1915 study by G. Ciamician²⁰. Wada et al.²¹ oxidized nicotine at 30 °C with pure O₂ and detected ammonia, methylamine, nicotinic acid, myosmine, cotinine and nicotyrine among the products. Linnell²² observed that the reaction with atmospheric oxygen was inhibited when nicotine was dissolved in acidified solutions, indicating that only the free base is involved in the oxidation. More recently, Mihranyan et al.²³ identified cotinine, nicotine-N-oxide, methanone-(1-methyl-3-pyrrolidinyl)-3-pyridinyl, myosmine and β -nicotyrine as degradation products during a 3-month storage study of nicotine adsorbed to cellulose powders.

Potential nicotine oxidation by atmospheric O₂ was not considered explicitly, but possibly contributed to the apparent irreversible behavior of sorptive sinks in at least one chamber study^{13, 24}. But most critically, these chamber tests were carried out under atmospheres generated either from ozone-free high-purity commercial air or by drawing ambient air through a combination of filters and activated carbon traps to remove ozone. That is a significant difference with respect to usual indoor environment conditions. Recently, atmospheric ozone has been recognized as a major driver of indoor chemistry^{25, 26}. Ozone generally enters the indoor

environment by ventilation or infiltration and is present at levels that are 20-70% of those in the entering outdoor air²⁵. It may also be generated in substantial quantities from devices marketed as “air purifiers”. The reaction of ozone with common indoor VOCs can be a source of irritant chemicals, ultrafine particulate matter and OH radicals²⁶⁻²⁹. It can also be removed by surface materials (carpet, wallboard)³⁰⁻³², in many cases through reactions that yield volatile aldehydes with low odor or irritation thresholds³².

Heterogeneous chemistry at environmental surfaces plays a key role in the transformation of pollutants associated with mineral and organic aerosol particles³³⁻³⁸, and is potentially critical to understand the transport and fate of low-volatility chemicals in indoor environments where the surface-to-volume ratio is significantly larger than in outdoor air. In that context, nicotine is a particularly good probe for ozone surface chemistry involving reversibly sorbed species, especially since it reacts relatively slowly with ozone in the gas phase, as estimated from reaction rates for structurally related amines (discussed below). In addition, its unusually high affinity for surfaces¹⁷ allows for its long-term exposure to atmospheric oxidants.

This study is motivated by the need to improve the accuracy of ETS exposure assessment. Our principal hypothesis is that reaction of sorbed nicotine with indoor ozone can reduce significantly the amount of alkaloid desorbed from surfaces. Those re-emissions were identified as a source of biases when nicotine was used as ETS tracer. We investigated nicotine desorption in dry and humid air from two model surfaces, Teflon and cotton, which have different effective surface area, hydrophilicity and chemical composition. In addition, identification of oxidation byproducts provided insight on the links between sorption, reactivity, and acid-base interactions.

Methods

Chamber design and measurements

Experiments were conducted in a modular chamber constructed with six gypsum wallboard panels (1.2 cm thick) tightly held together by an adjustable metal frame, inspired in a similar design by Waiman et al.³⁹. Inner dimensions were 56.3 x 57.0 x 64.0 cm³, surface area of 2.09 m² and surface to volume ratio of 10.2 m⁻¹. Internal wallboard surfaces were covered with a FEP-Teflon-lined bench protector (Saint-Gobain Corp, NJ). Unions between the panels were sealed with aluminum adhesive tape and internally masked with Teflon tape. Thus, all internally exposed surfaces were Teflon. The modular design allowed for opening and resealing of the chamber to introduce and remove surface materials between experiments. Two inlet ports, located on opposite corners 2-3 cm above the bottom, were used to introduce clean supply air with and without ozone, and nicotine vapor (Figure 1). Air exiting through a single port was directed to a secondary chamber for monitoring of temperature and RH, and then vented to a fume hood. Ideal mixing was verified during offline experiments by continuous monitoring of SF₆ at the outlet following injection into either inlet.

The reaction chamber and ancillary setup were housed in a 70-m³ lab provided with central air handling. Temperatures during the experimental period ranged from 21.5 to 22.5 °C, with fluctuations between 0.5 and 1.0 °C during each run. A clean air generator (AADCO 737-R) fed two air streams at 5 L min⁻¹ (\pm <1%) each. The primary supply stream was directed continuously to one of the chamber inlet ports. For experiments requiring humidified air, this stream was bubbled through deionized water (Millipore, R = 18 MΩ.cm). For experiments with ozone, an additional 100 cc min⁻¹ fed from a “zero” (i.e., high purity) air cylinder was directed through a Pen-Ray UV ozone source and joined to the primary air stream.

The secondary air stream passed over a diffusion tube containing liquid nicotine (>99%, Aldrich) in a vessel maintained at room temperature in a water bath. The nicotine supply rate was determined gravimetrically as $0.046 \pm 0.005 \text{ mmol h}^{-1}$ throughout all experiments. The nicotine-containing air stream was connected to the second inlet port only during the sorption phase of each experiment; otherwise it was directed to a fume hood. Thus, total airflow to the chamber was 10 L min^{-1} (3 air changes per hour, h^{-1}) during the sorption phase and 5 L min^{-1} (1.5 h^{-1}) during the desorption phase.

The ozone supply rate was $0.030\text{--}0.033 \text{ mmol h}^{-1}$, corresponding to a chamber steady-state concentration of $56 \pm 3 \text{ ppbv}$ in the absence of nicotine for an $\text{ach} = 1.5 \text{ h}^{-1}$. Ozone was measured in the supply airstream immediately before and at the conclusion of each experiment using a continuous monitor (API-400). During experiments ozone was monitored continuously at the chamber outlet.

Samples for chemical analysis were collected via a stainless steel 4-port union located just above the outlet port. Nicotine and other organic gases were sampled on Tenax-TA sorbent tubes using peristaltic pumps at variable flow rates; sample-specific flow rates were measured to within $\pm 0.5\%$. Volatile carbonyls were collected on DNPH-coated silica cartridges preceded by an ozone scrubber (Waters).

Tenax sorbent tubes were analyzed using either of two thermal desorption-gas chromatography (TD/GC) systems: a Hewlett Packard 5890 equipped with a Perkin-Elmer ATD 400 automatic multi-tube desorber with stainless steel tubes (Supelco) and a nitrogen-phosphorus detector (NPD), or a Hewlett Packard 6890 equipped with a Chrompack TCT 4020 desorber with cryogenic trap and glass sorbent tubes (Varian) and a 5973 mass selective detector (MSD) operated in electron impact mode. This allowed for more frequent sampling and therefore

improved time-resolution for selected experiments. Operating parameters for the GC-MSD system have been described previously¹⁸. Nicotine was quantified using multi-point calibrations referenced to internal standards: quinoline for GC-NPD and 1-bromo-4-fluorobenzene for GC-MS. Standard injections in the ranges 5-120 ng (NPD) and 20-150 ng (MSD) yielded linear calibration relationships. A group of 50 duplicate samples had an average percent standard deviation for nicotine concentration of 12.9 % and a median of 8.6 %. Several oxidation products were identified using authentic standards: N-methyl formamide (Aldrich, 99 %), nicotinaldehyde (or 3-pyridinecarboxaldehyde, Aldrich 98 %) and cotinine (Sigma, 98 %). Identification of other products was assisted with GC/MS spectral libraries.

DNPH-coated cartridges were extracted with 2 mL acetonitrile and analyzed by HPLC with diode-array UV-visible detection (HP1090) following the ASTM D 5197 method⁴⁰.

We designed a matrix of eight experiments to evaluate nicotine desorption by exploring the combination of three experimental variables: surface material (Teflon or cotton), presence or absence of ozone and the use of dry or humid air (at 65-70 % RH). Each experiment had both a sorption and desorption phase. The chamber was pre-conditioned at the desired RH (~0 % or 65-70 %), and the sorption phase was initiated by connecting the nicotine flow. In selected experiments, samples were collected during the initial hours of the sorption phase. The system was allowed to run at steady state for a period of 12 to 24 h, during which the nicotine concentration was monitored. Steady-state nicotine concentrations were 1.5-2.0 ppm (10-14 ng mL⁻¹). The desorption phase was initiated by disconnecting the nicotine source from the chamber and, in the experiments where ozone was used, connecting the ozone source to the chamber at the same time. Ozone was not introduced in the chamber during the sorption phase. Sorbent tubes samples were collected at intervals consistent with the anticipated nicotine concentration

change over one week, except in the experiments with ozone and Teflon surfaces, in which the nicotine concentration dropped at a much faster rate and reached our detection limit on the third day.

The cotton cloth was a common uncolored, untreated material that was preconditioned only by washing with hot water (with no detergent) and machine drying. A rectangular piece of 58.2 x 75.5 cm (85.9 g) was attached to two of the internal walls inside the chamber, in a position that was symmetric with respect to both inlets and the outlet. For each experiment with ozone, a new cotton sample of the same dimensions (< 0.1 % mass difference) was utilized

Surface characterization

The effective areas exposed to nicotine in the Teflon film and in the cotton cloth were estimated by determination of their corresponding N₂-BET surface areas. Small samples of each material (420 and 130 mg, respectively) were conditioned in a N₂ stream for 24 hours prior to analysis in a degasser (FlowPrep 060, Micromeritics). The BET-surface measurements were carried out with a surface gas adsorption analyzer (TriStar 3000, Micromeritics) via sample equilibration over a range of N₂ pressures at 77 K.

Water uptake capacity was determined by measuring the mass change of a small sample of each material (roughly 10 cm²), exposed first to dry air and subsequently to humid air at 70% RH. Both samples were placed together inside the RH monitoring chamber and equilibrated in a flow of 5 L min⁻¹ of dry air for two days. After weighing, the samples were replaced in the equilibration chamber and exposed to humidified air for 72 hours, from which they were removed briefly for weighing at 24, 48 and 72 h. Finally, the samples were exposed to dry air for two days and re-weighed to evaluate possible mass changes (hysteresis) by comparison to the initial mass. In all cases, the samples were preserved in a sealed petri dish after removal from the

exposure chamber and weighed within 2 min. Experimental error associated with transient water evaporation or absorption during this process was estimated as $< 2\%$ of the sample mass change for cotton and was below our limit of detection for the Teflon sample.

Results and Discussion

The key results of this work are displayed in Figures 2-3, which show the measured gas phase concentrations during the sorption (Fig. 2) and desorption (Fig. 3) phases of experiments with Teflon and cotton materials. Data are plotted as circles and squares for dry and humid air, respectively. In each figure, the time-concentration pattern for an ideal, non-sorbing compound is shown as a solid line that accounts for the air exchange rate. Deviations from this behavior result from sorption processes.

Sorption of nicotine on Teflon and cotton

Figure 2 shows that substantially more nicotine sorbed when cotton was present (Fig 2-B and 2-C), compared to Teflon (Fig 2-A). The extent of sorption is indicated by the difference between the ideal non-sorptive concentration curve and the experimental data. The measured nicotine profile differed slightly from non-sorptive behavior in the Teflon chamber, reaching steady state within 2 hours. The presence of water vapor did not influence nicotine uptake by Teflon. In contrast, nicotine did not reach steady state concentrations in the presence of cotton for ~ 6 hours under dry air (Fig 2-B) and more than 15 h under humid air (Fig 2-C). The attainment of steady state gas-phase concentrations reflects a balance between sorption and desorption mass transfer between the chamber air and surface sinks.

The presence of a second, slower sink (associated with either physical or chemical processes) could allow for ongoing mass transfer from air to the material without affecting gas-

phase concentrations at time scales much shorter than the residence time in the slow sink. This possibility is discussed later through direct analysis and is being investigated by mathematical modeling of sorption in the experiments; that modeling is the intended subject of a future publication in this series.

Estimates of the mass of nicotine sorbed to surfaces under each condition M_{sorb} (mg) result from application of equation 1,

$$M_{sorb} = \int_0^{t_{sorb}} f(C_{id} - C)dt \quad (1)$$

where f ($\text{dm}^3 \text{ min}^{-1}$) is airflow through the chamber, $C(t)$ (mg dm^{-3}) is the nicotine gas phase concentration, $C_{id}(t)$ (mg dm^{-3}) represents ideal, non-sorbing behavior and t_{sorb} (min) is the duration of the sorption phase. Areas under the experimental and ideal non-sorptive curves were calculated numerically and used in equation 1 to obtain $M_{sorb} = 0.3 - 0.9$ mg for Teflon under humid air, 12-18 mg for cotton under dry air and 33 – 57 mg for cotton under humid air. The midpoints of these ranges suggest that nicotine sorption to cotton was a factor of ~ 25 (under dry air) and ~ 75 (under humid air) greater than to Teflon. Large relative uncertainties in the calculated M_{sorb} values stem from the small relative difference between experimental and non-sorptive curves for Teflon, and from substantial variability in the measured values in the cotton experiments. The range of variability is illustrated in Fig 2-B and 2-C with two fitted curves for the cotton data, showing the higher and lower limits.

The substantially higher mass of nicotine sorbed to cotton compared to Teflon cannot be explained purely by surface area differences. Table 1 shows that the measured N_2 -BET surface of cotton, when expressed as cm^2 per unit exposed area, was only 3.6 times greater than the Teflon film lining the chamber interior. This is probably due to the higher porosity of the cotton fabric. The surface area for cotton ($1.17 \text{ m}^2 \text{ g}^{-1}$) was comparable to literature values for carpet

and a sofa (1.3 and $0.75 \text{ m}^2 \text{ g}^{-1}$ respectively) ⁴¹, as well as for cellulose powders of varied crystallinity ($0.48 - 1.18 \text{ m}^2 \text{ g}^{-1}$) ²³. The amount of nicotine sorbed per unit of BET surface area is estimated to be ~ 7 times greater for cotton (in dry air) than for Teflon. The even larger mass sorbed to cotton under humid air cannot be directly correlated with effective areas measured under anhydrous conditions, but it indicates considerable enhancement of sorption due to co-sorbed water. Acid/base interactions are expected when amino groups on nicotine interact with OH groups on the cellulosic backbone of cotton. In the presence of an aqueous film on cotton, greater uptake of nicotine can result from dissolution of the nicotine, enhanced by hydrogen-bonding and/or ionization.

Desorption of nicotine in the absence of ozone

The filled symbols in Figure 3 show that gas-phase nicotine decreased at approximately the ventilation removal rate (straight line) during the first few hours. Deviation from the non-sorbing decay curve after this initial period indicate the increasing importance of desorption relative to ventilation removal. With Teflon (Fig 3-A), nicotine gas-phase concentration decreased by 99% before the impact of desorption was apparent. For cotton (Fig 3-B), the measured profile deviated from the non-sorptive decay curve when gas-phase nicotine was still $>10\%$ of the initial desorption phase concentration; this reflects the substantially higher rate of nicotine desorption (mass transfer to the gas phase) from cotton relative to Teflon. Both materials exhibited ongoing desorption for the entire experimental period and behaved similarly under dry and humid air conditions, even though cotton had absorbed substantial amounts of water when it was present. Mid-week nicotine concentrations were about 3 and 2 orders of magnitude below initial levels for Teflon and cotton experiments, respectively. Although the

exposed surfaces in the latter were not just cotton but a combination of cotton with the remaining exposed Teflon, the effect of cotton dominated and determined the extent of nicotine desorption.

Table 2 shows the decay rate constants k derived by fitting the natural logarithms of the measured gas-phase concentration profiles in Fig. 3 for $t > 25$ h to a straight line. Long-term gas-phase concentrations during the desorption phase depended directly on the net mass transfer or reemission rate of nicotine from surfaces reflecting the overall impact of desorption and ongoing re-sorption to materials in the chamber. In all four experiments without ozone, decay rate constants were in the range $k = 1.7 - 3.3 \times 10^{-4} \text{ min}^{-1}$ ($0.25 - 0.5 \text{ day}^{-1}$). For comparison, we calculated the decay of gas-phase nicotine concentrations after daily smoking occurred over several month-long periods in a furnished and carpeted 50 m^3 experimental room¹⁹. Gas-phase nicotine measurements were made for several weeks after smoking ended, while the room was provided with ozone-free air at 0.3 h^{-1} . These previously unpublished data yield a gas-phase nicotine decay rate constant of $3.3 \times 10^{-5} \text{ min}^{-1}$. The lower decay rate corresponds to a slower rate of desorption mass transfer in the furnished room. This difference is expected because materials present in the room included porous wallboard, upholstered and padded furniture and carpet that all have deep physical reservoirs for diffusion and sorption.

Relative humidity had minimal influence on the desorption profiles from both Teflon and cotton (Fig 3), despite considerable water uptake by cotton (Table 1). While Teflon did not show any measurable mass change, the cotton mass increased by 7.1 %. This cotton water uptake capacity is consistent with two recent independent studies in which the mass change of a cotton sample was reported for the whole humidity range^{42, 43}. These investigations found a mass change of $\sim 6\text{-}7\%$ to a cotton sample exposed to air at 70 % RH.

The mass of nicotine desorbed was calculated in each case as

$$M_{des} = \int_0^{t_{des}} fCdt - C_0V \quad (2)$$

where t_{des} (min) is the duration of the desorption phase, and the product C_0V (mg) corresponds to the mass present in the gas phase at $t = 0$. For Teflon surfaces, the calculated $M_{des} = 0.5$ and 0.6 mg for experiments in dry and humid air, respectively, are within the range estimated for sorbed mass M_{ads} . For cotton, the desorbed mass of nicotine was $M_{des} = 14$ mg in dry air and 13 mg in the presence of humid air, compared to $M_{sorb} = 12$ - 18 and 33 - 57 mg sorbed in dry and humid air respectively. The mass remaining on cotton surfaces at the end of the period would be emitted over a period of ~ 3 and ~ 140 days respectively, using the estimated midpoint M_{sorb} values, final desorption rates, and assuming negligible contribution of additional slow sinks.

Effect of ozone on nicotine desorption

In Figure 3, open symbols indicate experiments with added ozone. A dramatic change in the nicotine concentration profiles was observed with Teflon surfaces (Fig. 3-A) in both dry and humid air. After one day of desorption, re-emitted nicotine levels in the presence of ozone were more than 10 times lower than those recorded without ozone at the same point, and nearly 2 orders of magnitude lower after the second day. Nicotine concentrations dropped below limits of detection after 70 hours.

Addition of ozone influenced desorption from cotton surfaces (Fig 3-B) only in dry air, with concentrations lower than baseline experiments (in the absence of O_3) by an order of magnitude after ~ 100 h. In contrast, ozone did not reduce nicotine desorption from cotton in humid air. This result suggests that the presence of co-sorbed water prevented ozone from decreasing desorption mass transfer.

To explain these observations, we postulate that ozone reacted with sorbed nicotine and steadily reduced the amount of nicotine available for desorption. The reduction of gas-phase nicotine concentrations in the presence of ozone could not have been caused by gas-phase reactions that were slower than the ventilation rate. The bimolecular rate constant for the ozone-nicotine gas phase reaction is not available in the literature, but data exist for structurally related aromatic and aliphatic amines. As shown in Table 3, the data clearly suggest that the pyridinic environment in nicotine is non-reactive, and the pyrrolidinic ring has only moderate reactivity. Considering trimethylamine as a surrogate tertiary amine, at typical ozone indoor levels (20-40 ppb) the pseudo-first order rate constant for the reaction of gas phase nicotine with ozone would be $1.4 - 2.8 \times 10^{-2} \text{ h}^{-1}$, roughly an order of magnitude lower than typical air exchange rates⁴⁴, and two orders of magnitude lower than our experimental air exchange rate.

A simple kinetic scheme for gas phase (C) and sorbed (S) nicotine in the presence of ozone is given by:

$$\frac{dC}{dt} = -\lambda \cdot C + \frac{A}{V} k S \quad (3)$$

$$\frac{dS}{dt} = -k S - r S \quad (4)$$

where λ is the air exchange rate, A and V are the chamber area and volume, k is the net desorption rate constant (in min^{-1}), and r the pseudo first-order rate constants for the surface reaction between nicotine and ozone (in min^{-1}). The system of equations 3-4 can be solved analytically, obtaining the following general expression for nicotine gas-phase concentration C as a function of time:

$$C(t) = C_0 \exp(-\lambda t) + \frac{A}{V} \frac{k}{(\lambda - k - r)} S_0 \{ \exp[-(k + r)t] - \exp[-\lambda t] \} \quad (5)$$

with C_0 and S_0 the initial nicotine concentration in each phase. For the long time range (i.e., for $t > 25$ h), the parameter $(k + r)$ can be calculated directly from the slope of the $\ln(C/C_0)$ vs t curves, provided that $(k + r) \ll \lambda$. Hence, the steeper concentration decay with ozone with respect to baseline (no-ozone) curves is directly proportional to r (reported in Table 2). The ratio r/k gives a quantitative measure of the relative rates for the competing processes of desorption and reaction with ozone. During experiments in dry and humid air, the ozone reactions removed nicotine from Teflon surfaces at $r/k = 3.5$ and 4.2 respectively. For cotton surfaces in dry air, $r/k = 2.0$.

The pseudo-first order reaction rate r can be seen as the product of a bimolecular ozone-surface nicotine reaction rate constant $r_{O_3}^S$ (in $\text{ppb}^{-1}\text{min}^{-1}$) and a stable ozone gas-phase concentration $[O_3]$ (in ppb):

$$r = r_{O_3}^S [O_3] \quad (6)$$

Bimolecular rate constants were calculated for Teflon and cotton using average O_3 concentrations of 42 and 14 ppb respectively, resulting in a value of $r_{O_3}^S$ smaller by a factor of 2 for Teflon than for cotton when both were in dry air (Table 2). Thus, sorption of nicotine to the more strongly interacting material, i.e. cotton, did not provide the substrate any additional protection from oxidation with atmospheric ozone in dry air.

A contrasting result was the complete inhibition of ozone reaction with nicotine sorbed to cotton in humid air (65-70 % RH). This effect was likely related to the water uptake by cotton. Okubayashi et al.⁴³ determined that a monolayer of water was established on cotton in equilibrium with 30-40 % RH. Therefore, at our higher RH, the surface held more than one monolayer. The protective role of water could be due to either or both of these reasons:

- 1) Ozone decomposes in aqueous media, catalyzed by OH^- at $\text{pH} > 6$ ^{45, 46}. This reaction is also surface-catalyzed⁴⁷. The blank curve for cotton in humid air suggests that O_3 was consumed at the diffusion-controlled (i.e., maximum) rate during the initial 5 days of exposure in the absence of nicotine. The main product of alkali-catalyzed self-decomposition is the hydroxyl radical, which can also react with nicotine, unless it is scavenged.
- 2) Nicotine can be protected by reversible chemical association with co-sorbed water. A significant change in the electron density of nicotine that made it less susceptible to electrophilic ozone attack can be induced by protonation of its amino groups, or by hydrogen bonding. In dilute aqueous solution, nicotine is preferentially protonated in the methylpyrrolidinic N atom at pH lower than $\text{p}K_1 = 8.01$, and can only exist in the diprotonated form at pH near or below $\text{p}K_2 = 3.10$. Pankow et al.⁴⁸ showed that the acid-base behavior of nicotine (recorded as a ^1H NMR chemical shift of its *N*-methyl protons) was not significantly altered in systems with lower aqueous activity, such as water/glycerin (35/65) mixtures with respect to pure aqueous solution. By contrast, calculations performed using density functional theory, as well spectroscopic evidence, suggest that in the gas phase and in organic aprotic media, both amino groups exhibit a much closer basicity^{49, 50}. We do not have structural information to identify which of the two proposed mechanisms predominates in our system.

Figure 4 shows the ozone concentration profiles in (A) Teflon and (B) cotton experiments. The figure includes curves for blank runs in which ozone was introduced to the chamber without nicotine. Ozone followed the behavior expected for a non-reactive tracer in the presence of Teflon surfaces (Fig. 4-A). In sharp contrast, the blank runs with cotton (Fig. 4-B) showed a substantial and stable ozone removal rate over a period of tens of hours.

Notably, in the cotton blank exposures for about the first 40 hours ozone remained at levels similar to those observed in experiments with nicotine (~13-15 ppb). For this period the rate of ozone removal by surface deposition/reaction is calculated by mass balance using equation 7

$$k_{O_3} = \frac{\lambda([O_3]_o - [O_3])}{[O_3]} = 0.075 \text{ min}^{-1} \quad (7)$$

with a measured inlet concentration $[O_3]_o = 56$ ppb and a measured chamber air concentration $[O_3] = 14$ ppb. The fact that this rate applies for both wet and dry cotton, with or without nicotine present – i.e. for a range of chemical environments at the surface – suggests strongly that it is the mass transport-limited deposition rate. Our determined k_{O_3} is within the range reported for ozone deposition velocities over 16 different building products³⁰. Combining the calculated deposition rate with the measured gas-phase ozone concentration yields an ozone surface uptake rate $\partial[O_3]/\partial t = k_{O_3} [O_3] \approx 1 \text{ ppb min}^{-1}$ or $5.3 \text{ ng cm}^{-2} \text{ h}^{-1}$, assuming that the uptake occurs predominantly on the cotton. This result is comparable to values reported by Morrison and Nazaroff for carpet fiber ($0.71 - 7.4 \text{ ng cm}^{-2} \text{ h}^{-1}$), but lower than for carpet backing ($25.0 - 39.6 \text{ ng cm}^{-2} \text{ h}^{-1}$) and for whole carpet ($18.8 - 35.4 \text{ ng cm}^{-2} \text{ h}^{-1}$)³¹.

For both materials, when sorbed nicotine was present, ozone concentrations were reduced relative to blank experiments. For cotton this divergence began after 60 hours or later. Instead, ozone concentration increased steadily from the start of the desorption phase with Teflon, and ozone in the Teflon chamber reached ‘blank’ concentration at about 60 hours. The coincidence of this process with the decay of gas-phase nicotine (Fig. 3A) – which in turn reflects a decrease in desorption mass transfer – supports the hypothesis that ozone reacted with surface-sorbed nicotine. The significantly different shapes of the ozone curves associated with nicotine sorbed to Teflon and cotton (Figs. 4A-B) suggest that the ozone deposition/reaction was mass transport

limited for cotton but not for Teflon. The availability of surface-bound nicotine as a co-reactant controlled ozone removal in the Teflon experiments.

Nicotine-ozone surface chemistry

Figure 5 shows the gas-phase concentrations of the oxidation products N-methyl formamide, nicotinaldehyde (or 3-pyridinecarboxaldehyde) and cotinine for Teflon (A) and cotton (B) surfaces in dry air, along with the nicotine levels for the same experiments. On Teflon, the concentrations of oxidation products decreased steadily, as surface nicotine was depleted, while the levels of oxidation products generated at cotton surfaces were relatively constant during the desorption period. This is consistent with higher nicotine surface concentration present on cotton surfaces and with the stability of ozone levels during the cotton exposure, suggesting a quasi steady-state for the surface reaction. Cotinine data showed higher scatter than the other two products, probably due to its lower gas-phase concentration and likely higher affinity for sorption.

Formaldehyde formed during ozone interaction with nicotine on both surfaces. Extracts of DNPH-impregnated samplers collected during the Teflon/humid air experiment over the periods 6-20 h and 20-29 h yielded formaldehyde levels of 1.9 and 1.8 ppb respectively. Similarly, samples collected during the cotton/dry air study showed higher (4.1 ppb) levels during the first day of desorption (2-5 h), and fell to 1.9 ppb at the end of the period (97-101 h). Formaldehyde concentrations in the blanks were negligible for Teflon, but were in the order of 0.7 and 0.6 ppb for blanks collected in the presence of cotton from 3-5 h and 5-19 h, respectively. This is an indication of reactions of the cotton with ozone, or with ozone-related reactive species such as OH radical.

These results cannot be used to estimate indoor exposure to formaldehyde generated in surface reactions, because the surface-to-volume (S/V) ratio, air change rates and other dynamic parameters differ from those found in typical indoor environments. For that reason, the measured formaldehyde concentrations (higher than residual nicotine levels) should be considered only as an illustration of the potential for ETS-loaded indoor surfaces to act as long-term low-level sources of irritant and toxic VOCs originating from their reactions with ozone. Such emissions could be magnified by the deliberate use of ozone generators as “air purifiers” to remove ETS components, as was pointed out by Shaughnessy et al ⁵¹.

Figure 6 outlines a general mechanism for the ozone-nicotine reaction that provides a rationale for the observed gas-phase products. We adapted the approach of Tuazon et al ⁵² for ozone-trimethylamine gas-phase reactions. Ozonation mechanisms of tertiary amines in aqueous solution share the same basic principles ⁵³⁻⁵⁶. An initial electrophilic attack of ozone at the amino group yields an excited N-oxide that can decompose via CH₃ or hydroxyl radical loss. The first process leads to the formation of stable nitro and nitroso compounds (not observed) and oxidation products of the CH₃ radicals, including formaldehyde. The second pathway leads to the formation of two possible organic radicals, indicated as **I** and **II** in Fig 6. Reaction with O₂ and recombination lead to various possible stable oxidation products that include most of the observed species (indicated with a box in Fig 6). Additional multifunctional reaction products were tentatively identified by matching their mass spectra with library data. Those structures, shown on Figure 1S (supplementary information), are consistent with the proposed mechanisms, and probably originate in further oxidation and fragmentation of the parent structures shown in Fig 6.

The observed reaction products derived from ozone attack on the pyrrolidinic ring of nicotine. This observation lends support to the hypothesis that ozone oxidation of sorbed nicotine competes with its interaction with water, because both take place at the pyrrolidinic amino moiety. Acid-base or other molecular interactions that induce a change in the electron density on that group can effectively inhibit oxidation reactions that operate through electrophilic attack on the pyrrolidinic nitrogen atom. Von Sonntag and collaborators^{57, 58} described a detailed mechanism for the initial steps of the reaction of ozone with tertiary amines in aqueous solution, observing that only the free base reacts with O₃ at rates in the order of 10⁶ dm³ mol⁻¹ s⁻¹.

Implications for assessment of secondary tobacco smoke exposure

We have shown that surface ozone chemistry can potentially account for the removal of a significant fraction of sorbed nicotine. Modeling the long-term indoor dynamics of nicotine under realistic environmental conditions should incorporate chemical losses at surfaces. These have the potential for mitigating nicotine re-emission, thus attenuating possible biases in the assessment of ETS exposure. In addition, surface ozone-nicotine reactions may operate as secondary sources of VOCs such as formaldehyde or N-methylformamide. Understanding the influence of the nature of the surface material and the role of sorbed water on nicotine surface reactivity with ozone presents challenges that require further kinetic investigation and modeling.

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Table 1: Characterization of exposed surfaces

	Teflon	Cotton
N₂-BET surface		
per unit mass (m^2/g)	0.190 ± 0.008	1.17 ± 0.02
per unit exposed area (m^2/m^2)	$60 \pm 3.$	218 ± 4
Water uptake		
(%)	0.00 ± 0.01	7.1 ± 0.3

Table 2: Initial nicotine gas phase concentration (C_0), desorption rate constant (k), pseudo-first order reaction rates with ozone (r) and bimolecular reaction rates ($r^S_{O_3}$) determined in desorption experiments.

	Teflon		Cotton	
	Dry air	Humid air	Dry air	Humid air
<i>In the absence of O₃</i>				
C_0 (ppm)	1.49	1.46	1.59	1.61
$10^4 k$ (min ⁻¹)	2.2	1.7	2.7	3.3
<i>With O₃</i>				
C_0 (ppm)	1.59	1.72	1.68	1.79
$10^4 r$ (min ⁻¹)	7.7	7.3	5.4	0
$10^5 r^S_{O_3}$ (ppb ⁻¹ min ⁻¹)	1.8	1.7	3.8	0

Table 3: Bimolecular reaction rates of ozone with amines

	Gas phase ^(a,b,c) (cm ³ molecule ⁻¹ s ⁻¹)	Aqueous solution ^(d,e) (dm ³ mol ⁻¹ s ⁻¹)	
		protonated	free base
<i>Aromatic amines</i>			
pyridine	< 1.1 x 10 ⁻²⁰ 1.23 x 10 ⁻²⁰	0.01	3
2-methylpyridine	4.90 x 10 ⁻²¹	n.a.	n.a.
3-methylpyridine	1.20 x 10 ⁻²⁰	n.a.	n.a.
2,5-dimethylpyridine	5.43 x 10 ⁻²⁰	n.a.	n.a.
<i>Aliphatic amines</i>			
pyrrolidine	n.a.	23.2	n.a.
methylamine	7.4 x 10 ⁻²¹	n.a.	<1.40 x 10 ⁵
dimethylamine	1.67 x 10 ⁻¹⁸	< 0.13	19 x 10 ⁶
trimethylamine	7.84 x 10 ⁻¹⁸	n.a.	4.1 x 10 ⁶
butylamine	n.a.	< 0.02	1.70 x 10 ⁵
aniline	1.1 x 10 ⁻¹⁸	n.a.	90 x 10 ⁶

(a): Ref ⁵⁹(b): Ref ⁶⁰(c): Ref ⁵²(d): Ref ⁶¹(e): Ref ⁶²

Captions to Figures

Figure 1: Experimental setup used in nicotine sorption/desorption tests.

Figure 2: Nicotine sorption concentration profiles for (A) Teflon and (B, C) cotton surfaces under ● dry and ■ humid air. The solid curves correspond to the non-sorptive ideal behavior, and the dotted curves to fitting of the experimental data showing higher and lower limits.

Figure 3: Nicotine desorption from (A) Teflon and (B) cotton surfaces in ● dry air, no O₃; ■ humid air, no O₃; ○ dry air in the presence of O₃; □ humid air in the presence of O₃. The solid curves correspond to the non-sorptive ideal behavior.

Figure 4: Ozone concentration profiles during nicotine desorption and in the absence of nicotine (blank runs). (A) Teflon surfaces; (B) cotton surfaces. The dotted lines indicate the range of concentrations expected in the absence of ozone surface deposition.

Figure 5: Gas-phase concentration of nicotine oxidation products: ○ N-methylformamide; □ nicotinaldehyde; Δ cotinine. Nicotine concentrations (●) are also indicated.

Figure 6: Suggested mechanism for the oxidation of surface nicotine by ozone. Byproducts indicated with a solid box were positively identified; those indicated with a dotted box were tentatively identified.

Figure 1S: Tentative identification of nicotine multifunctional oxidation products.